

PATENT SPECIFICATION

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NO DRAWINGS

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(54) CONCENTRATED SOLUTIONS OF CYCLAMMONIUM DYE SALTS, THEIR PRODUCTION AND USE

(71) We, J. R. GEIGY A.G., a body corporate organised according to the laws of Switzerland, of 215 Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns concentrated solutions of cyclammonium dye salts, a process for the production thereof and a process for the dyeing or printing of organic material, especially of acid modified synthetic textile fibres with the aid of the new solutions of dye salts according to the invention.

It is known that an unpleasant development of dust is involved in the handling and use, such as weighing, pouring, charging or dissolving, of dyestuffs, particularly the very strongly coloured cationic dyestuffs, in the form of powders. This dust formation is not only regarded as unpleasant and unhygienic by the personnel using the dyestuff powders but also leads to the continuous pollution of localities, working places and apparatus. This means that corresponding protective measures have to be taken. The impurification of the air by dyestuff particles can lead to other materials liable to be coloured being spotted and, therefore, e.g. colourless textiles or textiles dyed in one shade can be made unusable. Apart from these disadvantages which are disruptive chiefly in the production and use of the dusty dyestuffs, also considerable material losses can be incurred due to dustiness.

In addition, it is often difficult to dissolve pulverulent cationic dyestuffs in water as they cannot be wetted well and form lumps on the addition of water. The preparation of dye liquors is thus made a more difficult and, very often, a time-consuming operation. It is necessary, therefore, that these disadvantages should be removed as completely as possible.

Various suggestions have already been made for this purpose. Thus, the recommendation that cationic dyestuffs should be offered com-

mercially in the form of more or less concentrated solutions has been made. For example, the corresponding free dyestuff bases have first been produced from the usual dye salts, the former have been reacted to form salts of water soluble carboxylic acids and concentrated solutions of these carboxylic acid salts have been made in an anhydrous or water containing organic solvent which can be mixed with water in any ratio such as polyhydric alcohols and their ethers or esters, polyethers, amides, lactones, nitriles, dimethyl sulphoxide, tetrahydrofuran or dioxan. A substantially less complicated method consisted in dissolving the ammonium bases of cationic dyestuffs in aqueous aliphatic acids such as acetic acid in the presence of a non-ionic dispersing agent. According to another known process, cationic dyestuffs in the form of their free bases or their organic or inorganic salts are dissolved in a lower α - or β -hydroxyalkyl-nitrile or α - or β -alkoxyalkyl-nitrile. These processes have the disadvantage that they can only be used for certain cationic dyestuffs which form stable dye bases such as triphenylmethane dyestuffs. The important class of cyclammonium azo dyestuffs which form instable dye bases cannot be used in this way. In addition, these processes are relatively expensive due to the large amount of solvent required. Also, the use of considerable amounts of the toxic nitrile compounds mentioned is not without danger. Finally, large amounts of such solvents can have an unfavourable influence on the dyeing behaviour.

Novel, concentrated solutions of cyclammonium dye salts have now been found which are substantially free from the disadvantages listed above, are stable on storing and are ready for direct use.

According to the present invention there is provided a 5 to 50% by weight solution of a cyclammonium dye salt, the cationic moiety of which is free from groups which dissociate acid in neutral water, in an aqueous solvent medium which comprises an aliphatic mono-

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carboxylic acid of 1 to 4 carbon atoms and optionally auxiliary substances, the solution being free from any liquid organic solvent for the dye salt other than the said acid, the concentration of the said acid in said solution being such that the whole of the dye salt is dissolved in the solvent medium.

Cyclammonium dye salts which can be used according to the invention are, e.g.: the cyclammonium azo dye salts which draw onto acid modified synthetic fibres, particularly acid modified polyacrylonitrile fibres, and which contain no groups which dissociate acid in the cationic moiety such as sulphonic or carboxylic acid groups, the dye salts of the arylazo and anthraquinone series with an external cyclammonium group and the benzo-1, 2-pyrene dye salts containing cyclammonium groups.

In a preferred embodiment, the solutions according to the invention contain usual salts of cyclammonium azo dyestuffs, e.g., the halides, sulphates, alkyl sulphates, aryl sulphates or zinc chloride double salts which, optionally, contain several identical or different hetero atoms. In particular, these are dye salts which correspond to the formula



In this formula

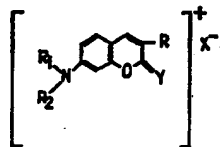
A represents the radical of an optionally benzo-condensed, N-quaternised azole or azine ring, preferably a thiazolium, benzo-thiazolium, imidazolium, benzimidazolium, pyridinium, quinolinium, pyrazolium, indazolium, triazolium or thiadiazolium radical,

B represents the radical of a coupling component containing no hydroxyl groups in a nucleus and no keto groups which can be enolised, especially a *p*-amino-phenyl, 4 - amino - naphthyl - (1), 3 - indazolyl, 3-indolyl- or 5-pyrazolyl radical, and

X⁻ represents an anion.

Amino-azo or amino-anthraquinone dyestuffs having an external pyridinium group in a substituent of the amino group are mentioned as dye salts of the arylazo and anthraquinone series with an external cyclammonium group.

As benzo-1,2-pyrene dye salts containing cyclammonium groups, the solution according to the invention can contain, e.g., dye salts of the formula



(II)

In this formula:

R represents an optionally benzo-condensed N-quaternised azole or azine ring, preferably a N-quaternised benzazole ring which is bound to the benzo - 1,2 - pyrene ring in a position adjacent the quaternary ammonium group.

R₁ and R₂ each represent hydrogen, an optionally substituted alkyl group or a cycloalkyl group, or R₁ and R₂ together with the nitrogen atom to which they are bound, optionally with the inclusion of a further hetero atom, represent a hetero ring; (preferably R₁ and R₂ are identical and represent alkyl groups having from 1 to 5 carbon atoms, especially the methyl or ethyl group),

Y represents =NH or =O and

X⁻ represents an anion.

The water-solubility of dye salts which can be used according to the invention depends on the nature of the anion X⁻.

The most suitable anion can easily be determined by prior tests. X⁻ can represent a methyl sulphate, ethyl sulphate, acetate, chloride, sulphate, phosphate or trichloride zincate anion.

The solutions according to the invention preferably contain 20—60% of said aliphatic monocarboxylic acids such as formic, propionic or butyric acid, solutions which comprise 20—60% and, preferably, 25—50%, of acetic acid being most preferred.

As further additives, the solutions of cyclammonium dye salts according to the invention may contain all metal complex-formers which form stable, water soluble, colourless complexes with any metal ions present in the concentrated dyestuff solutions. Suitable complex-formers are inorganic compounds such as water soluble polyphosphates or polymetaphosphates, preferably however organic compounds such as basic nitrogen compounds which contain at least two carboxymethyl groups bound to the nitrogen and which, optionally, are further substituted. Examples thereof are nitrilotriacetic acid, ethylenediamine tetraacetic acid, β-hydroxyethyl - ethylenediamine triacetic acid, cyclohexylenediamine tetraacetic acid or diethylenetriamine pentaacetic acid or the water soluble salts of these acids. In addition polycarboxylic acids containing hydroxyl groups such as citric or gluconic acid can be used as complex-formers.

In addition, the solutions according to the invention may contain, as further additives, normally said stabilisers, particularly non-ionic stabilisers such as surface active ethylene oxide addition products of organic hydroxyl, carbonyl, amino or amido compounds or mixtures of such substances having aliphatic hydrocarbon radicals with, in all, at least 8 carbon

atoms. Polyglycol ethers obtained from alkanols, alkenols, alkylphenols or fatty acids, optionally condensed with primary or secondary mono- or poly- basic amines, which have aliphatic hydrocarbon radicals with, in all, at least 8 carbon atoms, and, at least, 4 equivalents of ethylene oxide, are preferred. Addition products of 4 to 20 mols of ethylene oxide to an alkanol having 8 to 18 carbon atoms such as hexadecanol, the fatty alcohol mixture known by the generic term "coconut oil fatty alcohol", or to an alkyl phenol the alkyl moiety of which has, in all, at least 8 carbon atoms, e.g. to octyl phenol, nonyl phenol or di-tert.butyl phenol, are particularly suitable.

The amount of cyclammonium dye salts in concentrated solutions according to the invention is 5 to 50% by weight and, preferably, 10 to 35% by weight, calculated on the total weight of the solution.

The amount of the monocarboxylic acid should be, at least, sufficient to dissolve the whole of the cyclammonium dye salt. To fulfil this condition generally requires that at least 50% by weight and, advantageously, 65 to 90% by weight of the monocarboxylic acid as defined.

The amount of metal complex-former and/or stabiliser in solutions according to the invention may be 0.1 to 4% by weight, preferably however, 0.1 to 1% by weight of metal complex-former and/or 1 to 3% by weight of stabiliser calculated on the total weight of the solution.

The solutions according to the invention are produced, advantageously by stirring one or more of the cationic dyestuffs, preferably in the form of a moist filter cake or as powder or aqueous solution or suspension, into an aqueous monocarboxylic acid having 1 to 4 carbon atoms at room temperature and then optionally heating until a clear solution is attained, preferably to not over 50°C, using the usual technical mixing apparatus such as automatic stirrers or high velocity stirrers. In many cases it is advantageous then to clarify by filtration the solution from any inorganic residues present. As salts of cyclammonium azo dyestuffs which can be used according to the invention are meant both the dye salts obtained direct in the production of the dyestuff as well as the dye salts obtainable by double reaction, preferably with an alkali or ammonium salt, e.g. the chlorides obtained by reaction of methyl or ethyl sulphates with sodium chloride.

Solutions according to the invention are ready-for-use dye preparations which are stable on storing. Diluted with water (advantageously in a ratio of the least 1:10), they can be used direct as liquor for the dyeing or printing of organic materials such as leather, wool, silk, cellulose acetate, tanned cotton, paper and, particularly textile material made from acid modified synthetic fibres such as acid modi-

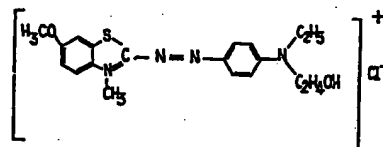
fied polyamide, polyurethane, polypropylene and polyester fibres, particularly however, from acid modified polyacrylonitrile fibres.

In addition, by the addition of suitable thickeners, thickened dyestuff solutions can be obtained which are excellently suitable for use in continuous dyeing or printing process.

The following Examples illustrate the invention. The temperatures are given therein in degrees Centigrade.

EXAMPLE 1

33.5 g of dried and milled dye salt of the formula

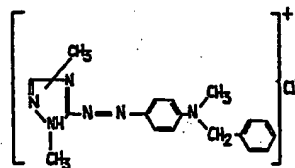


are slurried at room temperature with 60 ml of glacial acetic acid and 240 ml of 45–50° warm water are added while stirring. The solution formed is then left to stand for 14 hours at room temperature, after which slight quantities of inorganic residues are removed by filtration.

The dark blue concentrated solution produced in this way remains stable on storing and is ready for direct use. On pouring the solution into 50 to 100 times the amount of cold or warm water and adding the auxiliaries usual in dyeing, a liquor is obtained which can be used direct for the dyeing of acid modified polyacrylonitrile fibres such as "ORLON" (Registered Trade Mark) from a short liquor.

EXAMPLE 2

167 g of moist dyestuff filter cake containing 39 g of dye salt of the formula



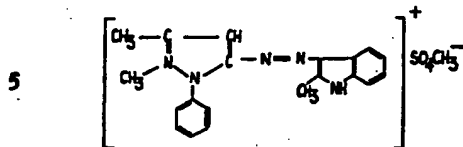
are added while stirring to 96 ml of glacial acetic acid and kept at 45–50° until a clear solution is formed. The solution formed is left to stand for 14 hours at room temperature and then slight amounts of inorganic residues present are removed by filtration.

The concentrated deep red solution obtained in this way remains stable on storing and is ready for direct use. On diluting the dyestuff solution with 50 to 100 times the amount of cold or warm water and with the addition of the auxiliaries usual in dyeing a dyebath is obtained which can be used direct for the dye-

ing of acid modified synthetic textile fibres,
e.g. acid modified polyacrylonitrile fibres.

EXAMPLE 3

20 g of the dye salt of the formula

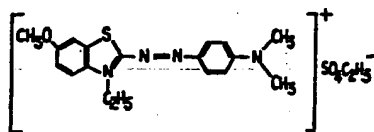


are slurried with 33 ml of glacial acetic acid and 66 ml of water at 65–70° are added while stirring. The solution formed is left to stand for 14 hours at room temperature and slight quantities of inorganic residues are removed by filtration. A ready-for-use, concentrated, yellow dyestuff solution is obtained which remains stable on storing.

If, instead of 33 ml of glacial acetic acid, 33 ml of formic acid 85%, or 50 ml of propionic acid are used and otherwise the procedure given in this Example is followed, then dyestuff solutions are obtained which have similar good properties.

EXAMPLE 4

100 g of the dye salt of the formula

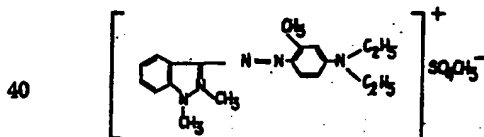


are added to a mixture of 300 ml of glacial acetic acid and 600 ml of water and dissolved by stirring. 5 g of ethylenediamine tetraacetic acid are added to the solution obtained. This solution is left to stand for 8 hours at 20–25° and is then clarified by removal of slight quantities of inorganic residues by filtration.

The deep blue dyestuff solution produced in this way remains stable on storing and is ready for direct use. On pouring the dyestuff solution into 50 to 100 times the amount of water containing thickener, a liquor is obtained which is suitable for the continuous dyeing of polyacrylonitrile fibres.

EXAMPLE 5

100 g of dried and milled dye salt of the formula



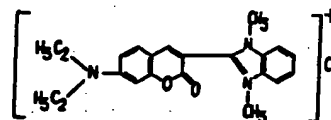
are dissolved by stirring at room temperature in a mixture of 150 ml of glacial acetic acid and 350 ml of water. 1 g of a condensation product of *p*-tert.amyl phenol and 15 mols of ethylene oxide is added to the solution obtained. This solution is left to stand for 8 hours at 20–25° and then slight quantities of inorganic residues are removed by filtration.

The violet concentrated dyestuff solution obtained in this way is stable on storing and ready for direct use. On adding 50 to 100 times the amount of cold or warm water to the dyestuff solution and on the addition of auxiliaries usual in dyeing a liquor is obtained which is particularly suitable for the dyeing of polyacrylonitrile fibres from a short liquor.

If instead of 1 g of a condensation product of *p*-tert.amyl phenol and 15 mols of ethylene oxide, 2 g of a nonyl phenol polyglycol ether having 8 to 12 ethyleneoxy groups or 2 g of a condensation product of oleyl alcohol and 25 mols of ethylene oxide are used and otherwise the procedure given in this Example is followed, then a dyestuff solution is obtained which has similar good properties.

EXAMPLE 6

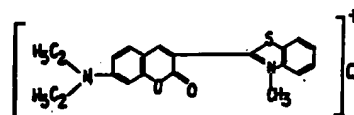
245 g of the dye salt of the formula



are dissolved by stirring in a mixture consisting of 620 ml of glacial acetic acid and 380 ml of water at room temperature. A deep yellow, ready-for-use dyestuff solution is obtained which is stable to storing. On diluting this with 1000 times the amount of water and after addition of auxiliaries usual in dyeing, a vivid yellow liquor is obtained which can be used direct for the dyeing of polymeric or copolymeric acrylonitrile textile fibres.

EXAMPLE 7

103 g of the dye salt of the formula



are dissolved by stirring and heating to 45° in a mixture consisting of 480 ml of glacial acetic acid and 480 ml of water. A deep yellow dyestuff solution which remains stable on storing is obtained.

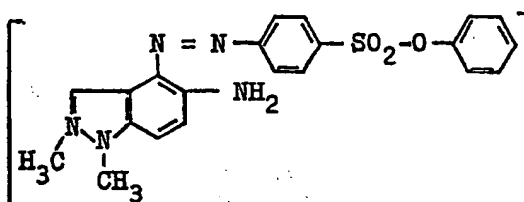
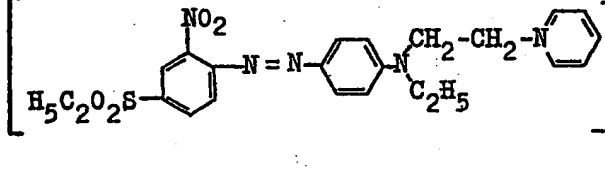
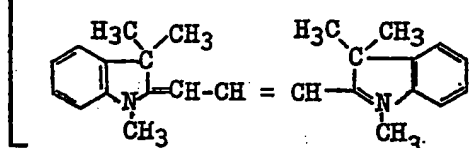
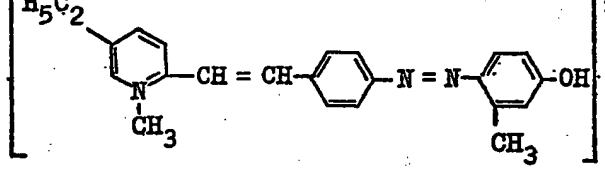
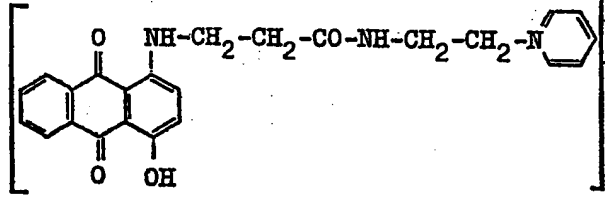
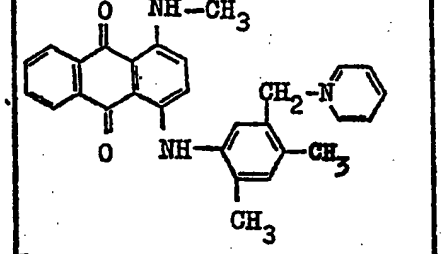
If in the above Examples, the dye salt component is replaced by corresponding amounts of the cationic dyestuffs given in column 2 of the following Table and otherwise the procedure given in Examples 1 to 7 is followed,

then dye preparations are also obtained which are ready for direct use and which remain stable on storing.

T A B L E

Ex.	cationic dyestuff	shade on polyacrylo- nitrile fibres
8	$\left[\begin{array}{c} \text{S} \\ \\ \text{C}_5\text{H}_4\text{N}^+\text{CH}_3 \\ \\ \text{N} = \text{N} - \text{C}_8\text{H}_6\text{N}^+\text{H} \end{array} \right]^+ \quad \text{Cl}^-$	red
9	$\left[\begin{array}{c} \text{H}_3\text{C} - \text{C} - \text{CH} \\ \quad \\ \text{H}_3\text{C} - \text{N} - \text{C} \\ \\ \text{C}_6\text{H}_5 \end{array} - \text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{N}^+(\text{CH}_3)_2 \right]^+ \quad \text{CH}_3\text{SO}_4^-$	red
10	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{N} - \text{N} \\ \quad \\ \text{H}_3\text{C} - \text{S} - \text{C} = \text{N} - \text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{N}^+(\text{CH}_3)_2 \end{array} \right]^+ \quad \text{Cl}^-$	violet
11	$\left[\begin{array}{c} \text{H}_3\text{C} - \text{C} - \text{CH} \\ \quad \\ \text{H}_3\text{C} - \text{N} - \text{C} \\ \\ \text{CH}_3 \end{array} - \text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{N}^+(\text{CH}_3)_2 \right]^+ \quad \text{CH}_3\text{COO}^-$	scarlet
12	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{N} - \text{N} \\ \quad \\ \text{C}_5\text{H}_4\text{N}^+\text{CH}_3 \end{array} - \text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{NH}_2 \right]^+ \quad \text{ZnCl}_3^-$	orange
13	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_8\text{H}_6\text{N}^+\text{CH}_3 \\ \\ \text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{N}^+(\text{CH}_3)_2 \end{array} \right]^+ \quad \text{NaSO}_4^-$	violet

Ex.	cationic dyestuff	shade on polyacrylo- nitrile fibres
14	$\left[\text{pyridine-2-yl-N(CH}_3\text{)} = \text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{N(CH}_3\text{)}_2 \right]^+ \text{H}_2\text{PO}_4^-$	violet
15	$\left[\text{2-methyl-4-(2-ethyl-1H-imidazol-5-ylthio)phenyl} = \text{N} = \text{N} - \text{2-ethyl-1H-imidazole} \right]^+ \text{Cl}^-$	orange
16	$\left[\text{2-methyl-2-(2-ethyl-1H-imidazol-5-ylthio)propan-1-yl} = \text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{N(C}_2\text{H}_5\text{)}_2 \right]^+ \text{ZnCl}_3^-$	red
17	$\left[\text{2-methyl-2-(2-amino-1H-naphthalen-1-ylthio)propan-1-yl} = \text{N} = \text{N} - \text{1H-naphthalen-1-yl} \right]^+ \text{CH}_3\text{SO}_4^-$	scarlet
18	$\left[\text{2-methyl-2-(2-chloro-6-(2,6-dimethyl-1H-imidazol-1-yl)phenylthio)propan-1-yl} = \text{N} = \text{N} - \text{C}_6\text{H}_4 - \text{N(CH}_3\text{)}_2 \right]^+ \text{Cl}^-$	red

Ex.	cationic dyestuff	shade on polyacrylo- nitrile fibres
19	 SO_4CH_3^-	yellow
20	 Cl^-	red
21	 Cl^-	red
22	 Cl^-	yellow-orange
23	 SO_4CH_3^-	red
24	 Cl^-	blue

Ex.	cationic dyestuff	shade on polyacrylonitrile fibres
25	$\left[\begin{array}{c} \text{H}_3\text{CO} \\ \\ \text{C}_6\text{H}_3\text{S} \\ \\ \text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{C}_2\text{H}_5)_2 \\ \\ \text{CH}_2\text{CH}_2\text{CONH}_2 \end{array} \right]^+ \text{Cl}^-$	blue
26	$\left[\begin{array}{c} \text{H}_3\text{CO} \\ \\ \text{C}_6\text{H}_3\text{S} \\ \\ \text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{C}_2\text{H}_5)_2 \\ \\ \text{CH}_2\text{CH}_2\text{CN} \end{array} \right]^+ \text{Cl}^-$	blue
27	$\left[\begin{array}{c} \text{S} \\ \\ \text{C}_4\text{H}_3\text{N} \\ \\ \text{CH}_2\text{CH}_2\text{CN} \end{array} \right]^+ \text{Cl}^-$	red
28	$\left[\begin{array}{c} \text{O}_2\text{N}-\text{C}_6\text{H}_3\text{N}(\text{CH}_3)-\text{N}=\text{N}-\text{C}(\text{CH}_3)=\text{N}-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_3\text{N}(\text{CH}_3)-\text{NO}_2 \\ \qquad \qquad \qquad \qquad \qquad \qquad \\ \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \end{array} \right]^+ \text{SO}_4^{2-}$	green
29	$\left[\begin{array}{c} \text{O}_2\text{N}-\text{C}_6\text{H}_3\text{N}(\text{CH}_3)-\text{N}=\text{N}-\text{C}_6\text{H}_3\text{N}(\text{CH}_3)_2 \\ \qquad \qquad \qquad \\ \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \end{array} \right]^+ \text{Cl}^-$	navy blue
30	$\left[\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ \quad \\ \text{C} \\ \\ \text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2 \\ \\ \text{CH}_3 \end{array} \right]^+ \text{SO}_4^{2-}$	red

Ex.	cationic dyestuff	shade on polyacrylo- nitrile fibres
31	 <chem>CN1C(=N2C(=CN(C)C2)C3=CC=CC=C3)C(=N4N(C)C5=CC=CC=C45)C6=CC=CC=C6</chem> Cl^-	orange
32	 <chem>CN1C(=O)C2=C(C(=C3C4=CC(=C(C=C4)Br)OC)C(=C5C6=CC(=C(C=C6)Cl)N(C)C5=O)C=C3C)OC</chem> SO_4CH_3^-	yellow

EXAMPLE 33

8 g of the dyestuff solution produced according to Example 1, 50 g of sodium sulphate and 10 g of an addition product of 15 to 20 equivalents of ethylene oxide and N-octadecyl diethylenetriamine which has been quaternised with dimethyl sulphate, are dissolved in 5000 ml of water. 100 g of polyacrylonitrile yarn ("ORLON" 42) are introduced at 60°, the liquor is heated within 10 minutes to 80°, the temperature of the liquor is then raised at the rate of $\frac{1}{2}$ a degree per minute until boiling is attained whereupon the material is left in the liquor at this temperature for 2 hours. The liquor is then cooled to 60° within 30 minutes. The material so dyed is then removed from the liquor and rinsed with lukewarm and cold water.

Polyacrylonitrile yarn dyed a very level blue colour is obtained.

On following the above prescription, the dyestuff solutions given in the other Examples produce dyeings of similar quantity on polyacrylonitrile fibres.

EXAMPLE 34

Polyacrylonitrile fabric such as "ORLON" 42, is impregnated in a foulard at 40° with a liquor of the following composition:

20 g of the dyestuff solution obtained according to Example 4 are dissolved in a thickener solution consisting of 5 g of locust bean flour thickener and 885 ml of water and then 30 g of coconut oil fatty acid diethanolamide are added to the solution.

The fabric, which has been squeezed out to about 120% liquor content, is steamed for 30 minutes at 102°. The dyed goods are rinsed with water, soaped and dried. Under these conditions, a very level yellow dyeing is obtained.

If in the above example, instead of polyacrylonitrile fabric, cellulose acetate fabric is used and otherwise the procedure given in the Example is followed, then a very level yellow dyeing is also obtained.

The dyestuff solutions described in the other Examples produce dyeings of similar quality by this process.

WHAT WE CLAIM IS:—

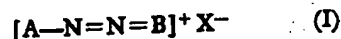
1. A 5 to 50% by weight solution of a cyclammonium dye salt, the cationic moiety of which is free from groups which dissociate acid in neutral water, in an aqueous solvent medium which comprises an aliphatic monocarboxylic acid of 1 to 4 carbon atoms and optionally auxiliary substances, the solution being free from any liquid organic solvent for the dye salt other than the said acid, the concentration of the said acid in said solution being such that the whole of the dye salt is dissolved in the solvent medium.

2. A solution according to claim 1 wherein

the dye salt is a cyclammonium azo dye salt.

3. A solution according to claim 1 or 2 wherein the dye salt is an optionally benzo-condensed azolium or azinium dye salt, optionally having several, identical or different, hetero atoms.

4. A solution according to claim 2 or 3 wherein the dye salt is a cyclammonium azo dye salt of the formula



wherein

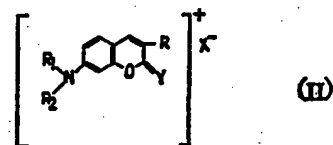
A represents the radical of an optionally benzo-condensed, N-quaternised azole or azine ring,

B represents the radical of a coupling component containing no hydroxyl groups in a nucleus and no enolisable keto groups, and

X⁻ represents an anion.

5. A solution according to claim 1 wherein the dye salt is a benzo-1,2-pyran dye salt containing a cyclammonium group.

6. A solution according to claim 1 or 5 wherein the dye salt is of the formula



wherein

R represents an optionally benzo-condensed, N-quaternised azole or azine ring which is bound to the benzo-1,2-pyran ring in a position adjacent the quaternary ammonium group,

R₁ and R₂ each represent hydrogen, an optionally substituted alkyl group or a cycloalkyl group, or R₁ and R₂ together with the nitrogen atom to which they are bound, optionally with the inclusion of a further hetero atom, can form a hetero ring,

Y represents =NH or =O, and

X⁻ represents an anion.

7. A solution according to claim 4 or 6 wherein the dye salt of formula I or II X⁻ represents a methyl sulphate, ethyl sulphate, acetate, chloride, sulphate, phosphate or trichloride zincate anion.

8. A solution according to any of claims 1 to 7, wherein the dye salt is dissolved in at least 50% by weight of the aqueous concentrated monocarboxylic acid having 1 to 4 carbon atoms.

9. A solution according to any of claims 1 to 8, which contains 20—60% aqueous acetic acid as the monocarboxylic acid ingredient.

10. A solution according to any of claims 1 to 9, which comprises 10 to 35% by weight of

a cyclammonium dye salt dissolved in 25 to 50% aqueous acetic acid.

11. A solution according to any of claims 1—10, which comprises a metal complex-former as further additive.

12. A process for the production of a solution of a cyclammonium dye salt as defined in claim 1, which comprises dissolving the dye salts and, optionally, further additives in at least one aqueous concentrated monocarboxylic acid which contains 1 to 4 carbon atoms.

13. A process according to claim 12, wherein 20—60% aqueous acetic acid is employed.

14. A process for the dyeing or printing of organic material using a solution as defined in any of claims 1 to 11.

15. A process according to claim 14 wherein the organic material is acid modified synthetic textile fibres.

16. A solution according to any of claims 1 to 10, substantially as described in any one of the foregoing examples 1 to 33.

17. A method of dyeing polyacrylonitrile fibres substantially as described in Example 34.

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